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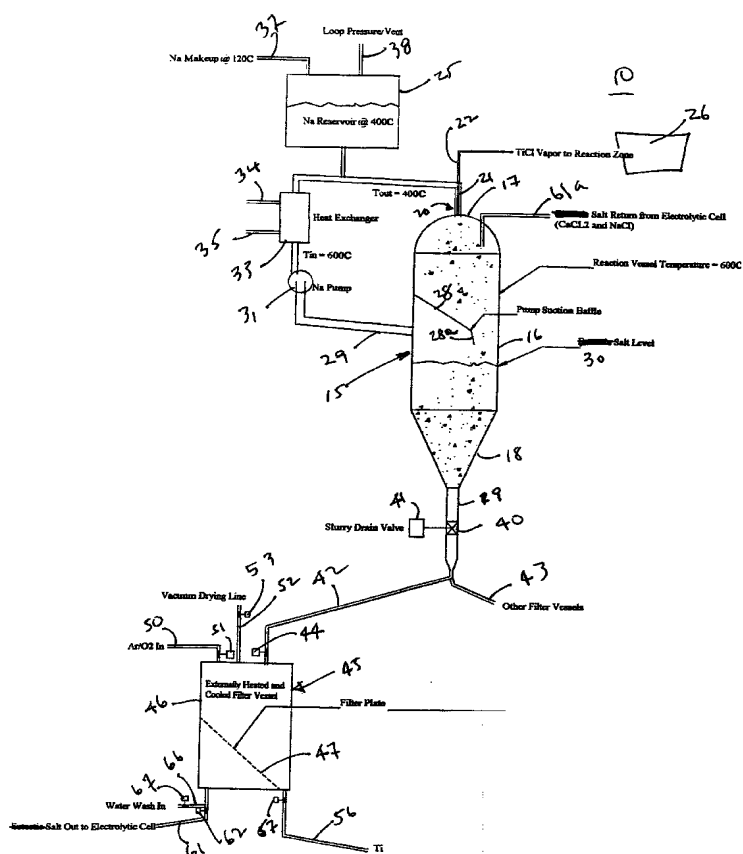
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3 September 2003 (03.09.2003)</p> <p>(25) Filing Language: English</p> <p>(26) Publication Language: English</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>60/408,932</td> <td>7 September 2002 (07.09.2002)</td> <td>US</td> </tr> <tr> <td>60/408,925</td> <td>7 September 2002 (07.09.2002)</td> <td>US</td> </tr> <tr> <td>60/408,933</td> <td>7 September 2002 (07.09.2002)</td> <td>US</td> </tr> </table> <p>(71) Applicant (<i>for all designated States except US</i>): INTERNATIONAL TITANIUM POWDER, LLC. [US/US]; 20634 W. Gaskin Drive, Lockport, IL 60441 (US).</p> | 60/408,932 | 7 September 2002 (07.09.2002) | US | 60/408,925 | 7 September 2002 (07.09.2002) | US | 60/408,933 | 7 September 2002 (07.09.2002) | US | <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (<i>for US only</i>): ANDERSON, Richard [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). ARMSTRONG, Donn [US/US]; 6005 Ridge Court, Lisle, IL 60532 (US). JACOBSEN, Lance [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).</p> <p>(74) Agent: LEVY, Harry, M.; Emrich and Dithmar, 300 South Wacker Drive, Suite 3000, Chicago, IL 60606 (US).</p> <p>(81) Designated States (<i>national</i>): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.</p> <p>(84) Designated States (<i>regional</i>): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW).</p> |
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[Continued on next page]

- (54) Title:** PROCESS FOR SEPARATING TI FROM A TI SLURRY



(57) Abstract: A method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates is disclosed. The metal and salt particulates are concentrated by removing at least some of the liquid metal, and then, liquid metal or a liquid of the original salt constituent or a mixture thereof is passed through the particulates at a temperature greater than the melting point of the original salt constituent to further concentrate the metal particulates. The metal particulates are then separated from the remaining original constituents or a mixture of the salt constituent. Density differences between the liquid metal and salt are also used to facilitate separation.



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ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
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ning of each regular issue of the PCT Gazette.*

PROCESS FOR SEPARATING TI FROM A TI SLURRY

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application serial No. 60/408,932, filed September 7, 2002, U.S. Provisional Application Serial No. 60/408,925, filed September 7, 2002 and U.S. Provisional Application Serial No. 60/408,933, filed September 7, 2002

BACKGROUND OF THE INVENTION

This invention relates to the separation of unwanted constituents from a slurry produced during operation of the Armstrong Process and method to produce a product as disclosed in U.S. patent nos. 5,779,761, 5,958,106 and 6,409,797 patents, the disclosures of which are herein incorporated by reference. As indicated in the above-identified and incorporated patents, the continuous process there disclosed, produces, for instance, titanium or a titanium alloy by the reduction of titanium tetrachloride with excess sodium. The product stream that exits the reactor is a slurry of liquid metal, salt particles or powder and titanium metal or metal alloy as particulates or powder. It should be understood that this invention relates to any material which can be made according to the Armstrong Process. When the slurry produced by the Armstrong Process is filtered, a gel or gel-like material is formed of the metal powder or particulates, the salt powder or particulates and the excess liquid reducing metal. This slurry has to be treated to separate the unwanted constituents, such as excess liquid metal, salt particulates from the desired end product which is the metal particulates or powder.

SUMMARY OF THE INVENTION

In developing the Armstrong Process with respect to titanium and its alloys, it has been found that the method of producing the slurry above referenced is very rapid and separation of the product from the slurry is the most difficult aspect in engineering of the continuous process. The description will be in terms of the exothermic reduction of titanium tetrachloride with sodium to produce titanium particles, sodium chloride particles and excess sodium; however, this is not to be

construed as a limitation of the invention but for convenience, only.

Accordingly, it is an object of the present invention to provide a method for separating metal powder or particulates from a slurry of liquid metal and metal powder or particulates and salt powder or particulates.

Yet another object of the present invention is to provide a method of separating metal particulates from a slurry of the type set forth in which one of the unwanted constituents is used to separate both constituents from the slurry.

A still further object of the present invention is to provide a method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates, comprising concentrating the metal and salt particulates by removing at least some of the liquid metal, passing the liquid metal or a liquid of the original salt constituent or a mixture thereof at a temperature greater than the melting point of the original salt constituent or mixture thereof through the concentrated metal and the particulates to further concentrate the metal particulates, and thereafter separating the metal particulates from the remaining original constituents or a mixture of the salt constituent.

A final object of the present invention is to provide a method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates, comprising introducing the slurry of original constituents into a vessel having a liquid salt therein wherein layers form due to density differences with the liquid metal being the lightest and the metal particulates being the heaviest increasing the concentration of the metal particulates toward the bottom of the vessel, removing liquid metal from the vessel, separating the concentrated metal particulates with some liquid salt from the vessel, filtering the salt from the metal particulates, and thereafter cooling and water washing the salt from the metal particulates.

Additional advantage, objects and novel feature of the invention will become apparent to those skilled in the art upon examination of the following and by practice of the invention.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and

particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic illustration of a first embodiment of the invention;

Fig. 2 is a schematic illustration of another embodiment of the present invention; and

Fig. 3 is a schematic illustration of another embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawings and more particularly to Fig. 1, there is shown a separation system 10 in which a vessel 15 has a generally cylindrical portion 16 with a dome shaped top 17 and a frustoconical shaped bottom 18 and exit pipe 19 extending from the bottom of the vessel 15. A reactor 20 of the type disclosed in the above-referenced patents has a outer liquid metal or sodium tube 21 and an inner halide vapor or titanium tetrachloride tube 22. A liquid metal or sodium supply tank 25 feeds sodium to the sodium or other liquid metal to the reactor 20 and a halide boiler 26 feeds the appropriate halide vapor to the reactor 20, all as previously described.

Internally of the vessel 15 is a downwardly sloping baffle 28 having a distal end 28a extending at a more acute angle and generally opposite to a sodium or liquid metal outlet 29. The liquid metal outlet 29 is in fluid communication with a metal or sodium pump 31 which leads to a heat exchanger 33 having a fluid inlet 34 and a fluid outlet 35. A liquid metal make-up line 37 is in communication with the supply tank or reservoir 25. A vent line 38 is provided in the tank or reservoir 25, as is well known in the engineering art.

A valve 40 with an actuator 41 is positioned in the exit 19 of the vessel 15 which is in communication with two exit lines 42 and 43, each of which being provided with a valve such as a valve 44 illustrated in line 42.

A filter assembly 45 includes a container 46 and a sloping filtered plate 47 for a purpose hereinafter set forth. A passivating gas inlet 50 has a valve 51 intermediate the source of passivating gas (not shown) and the container 46. A vacuum drying line 52 exits the container 46 and is provided with a valve 53. A slurry outlet line 56 at the bottom of the container 46 is provided with a valve 57 and a salt outlet line 61 is provided with a valve 62. Finally, a water wash inlet pipe 66 is provided with a valve 57.

The separation system 10 operates in following manner wherein material such as a metal or metal alloy is produced in the reactor 20 by the method previously described in the aforementioned and incorporated Armstrong patents.

By way of illustration only, titanium or a titanium alloy may be made by the reduction of titanium tetrachloride vapor or a plurality of halide vapors for an alloy by an alkali or alkaline earth metal such as sodium or magnesium. Alloys are easily made with the Armstrong Process by mixing the halide vapors in the appropriate quantities and reducing them in the exact same manner as hereinbefore described. In any event, using a large excess of the reducing metal to control the reaction produces a slurry of excess reducing metal, such as sodium, the metal particulates such as titanium and another reaction product such as salt particles, sodium chloride. The slurry leaving the reactor 20 may be at a variety of temperatures controlled, in one instance, by the amount of excess reducing metal present.

In an actual example, the slurry may typically have up to about 10% by weight particulates, and the particulates may be salt having diameters on average of from about 10 to about 50 microns and titanium having diameters on average in the range of from about 0.1 micron to about 500 microns, the titanium particulates or powder may be more likely to be in the range of from about 1-10 microns and the agglomerated ligaments (lumps) of the titanium in the range of between about 50 and about 1000 microns. This combination of liquid metal, salt particulates and titanium particulates leave the nozzle 20 and enter the vessel 15. The salt in the

vessel 15 is indicated to be at a level of which may be arbitrarily chosen so long as it is below the sodium outlet 29. The salt may be the reaction product salt, for instance sodium chloride, or a salt mixture which has a melting point lower than the reaction product salt. Although the salt may be as stated any salt, preferably the salt is the product of reaction or a mixture thereof, for instance an eutectic such as the calcium chloride- sodium chloride eutectic which melts at about 600°C.

The entire system 10 then may be operated at a lower temperature. For instance, sodium chloride melts at about 850°C. so if the salt in the vessel 15 is sodium chloride, then the vessel 15 must be operated above the melting point thereof, but as the eutectic melts at 600°C, this reduces the operating temperature.

In any event, irrespective of what salt is present at the level 30 in the vessel 15, the liquid metal will float due to density differences and be extracted through the outlet 29 by means of the sodium or liquid metal pump 31. A heat exchanger 33 having suitable inlet and outlet lines 34, 35 serves to reduce the temperature of the sodium out from the 600° in the vessel 15 (by way of example only) so that the recycled sodium enters the reactor 20 at a preselected temperature (for instance about 400°C). The baffle 28 and 28a prevents particulates entering the vessel 15 from the reactor 20 from being sucked into the sodium outlet 29.

As particulates settle in the lower portion 18 of the vessel 15, the particulate concentration is increased due to the removal of sodium through the line 29. Upon actuation of the valve 40, concentrated slurry will drain through the outlet or exit 19 through line 42 into the filter assembly 45. In the filter assembly 45, which is maintained by temperatures sufficient to keep the molten salt in a liquid phase, metal particles collect on the filter plate 37 while salt passing through the filter plate exits through line 61 to be returned, for instance, to an electrolytic cell (not shown).

The valve 62 opens the line 61 to permit the salt to drain while valve 57 is closed to prevent material from exiting the filter assembly 45. After a sufficient filter cake has been built up, the valve 62 is closed, the valve 44 is closed and the vacuum drying line 53 is opened after the filter cake has cooled to less than about 100 °C so that the passivating gas which may be argon and a small percentage of oxygen may be introduced into the container 46 by actuation of the valve 51. After the filter cake

which may be principally titanium powder with some salt is passivated, then the valve 51 is closed and the water wash valve 67 opened thereby allowing water to enter into the container 46 which both dissolves salt and moves the filter cake through line 56 to a finish wash and classification, it being understood that valve 67 will be opened prior to the water wash. The salt coming out of the filter assembly 45 through line 61 can be recirculated to the vessel 15 as indicated by the line 61a.

As seen therefore, the separation system 10 depends on the difference in gravity between the unwanted liquid metal constituent of the slurry and the salt and metal particulates produced during the reaction of the dried vapor and the reducing metal. Although this separation system 10 is a batch system, it can be rapidly cycled from one filter assembly 45 to other filter assemblies as needed through a simple valve distribution system, as is well known in the art.

Although the above example was illustrated with sodium and titanium tetrachloride, it should be understood that any material made by the Armstrong Process may be separated in the aforesaid manner.

Figure 2 shows an alternate embodiment separation system 80 in which a vessel 85 is similar to the vessel 15 and has a cylindrical portion 86, a dome top 87 and a frustoconical bottom 88 having an exit 89 extending therefrom. A reactor 90 of the same type as hereinbefore described is in communication with the vessel 85 and has a halide inlet 91 and a reducing metal inlet 92. A slurry outlet 93 which is in communication with the top 87 of the vessel 85. The filter 95 is any suitable filter, well known in the art, but preferably, for purposes of illustration only, is a "wedge screen filter" of a size to pass up to 125 micron particles. The material that flows through the filter 95 exits the vessel 85 through an output line 96 and flows into a gravity separator 97. The gravity separator 97 is frustoconical in shape and has an outlet 99 through which the heavier of the materials flows, in this particular case sodium chloride. An outlet 98 takes the lighter of the material, in this case sodium and recycles same through appropriate filters and other mechanisms, not shown, to the reactor 90. In this embodiment, the vessel 85 is maintained at an elevated temperature of about 850°C with either internal or external heaters, as is well known in the art, in order that the salt in this case, sodium chloride, is liquid or molten. The

molten sodium in large excess displaces the sodium chloride around the particulates and therefore the sodium and the salt flows through the filter plate 95 into the gravity separator 97 and is recycled as previously described. After a suitable filter cake is built up on the filter plate 95, the valves are closed and the filter cake is thereafter

removed for further processing. The advantage of the embodiment disclosed herein is that one of the unwanted constituents, that is the sodium liquid metal is used to displace the other unwanted constituent which in this case is the molten salt. Suitable heat exchangers are required to reduce the temperature of the exiting sodium in line 98 before it is recycled and to heat and maintain the temperature of the salt in the molten state in both the vessel 85 and in the vessel 97.

Referring now to Figure 3, there is another embodiment of the present invention illustrated as the separation system 100. The separation system 100 is provided with similar equipment as illustrated in embodiments 10 and 80. In the system 100, there is a vessel 105 having a cylindrical portion 106, a dome shaped top portion 107 and a frustoconical shaped bottom portion 108 having an exit 109 at the bottom thereof. A reactor 110 of the type described in the previously described for practicing the Armstrong process has, as for example only, a titanium tetrachloride inlet 111 and a sodium inlet 112 which serves to produce the reaction previously described with the outlet 113 carrying the slurry produced from the reaction.

A gravity separator 117 is frustoconical in shape and has an outlet 118 for the lighter weight liquid metal such as sodium and a bottom outlet 119 through which the heavier unwanted constituent, in the present case sodium chloride, exits. Suitable valves are provided between the exit line 116 and the gravity separator 117 as indicated by the valve 121 and a valve 122 is in the exit line 116 between the vessel 105 and the sodium inlet 112. Another valve 123 is intermediate the vessel 105 and the sodium chloride outlet from the gravity separator 117 and finally a valve 124 is intermediate the reactor 110 and the vessel 105.

In the present system 100, the filter plate 115 collects the metal particulates as the salt which is molten and at a suitable temperature such as greater than the melting points, such as 850°C. for sodium chloride flows through the filter plate 115

carrying with it excess molten sodium which is displaced from the filter cake as it builds on the filter 115. The combination of liquid sodium and liquid salt flows out of the vessel 105. Closing valve 122 and opening the valve 121 results in the material being moved by a suitable pump (not shown) to the gravity separator 117. In the gravity separator 117, the liquid metal sodium floats and the liquid salt forms the heavier layer at the bottom of the separator 117 and is separated as indicated with the sodium being drawn off at the top of the separator through line 118 to be recycled (after cooling if required) to the sodium inlet to the reactor 110. The salt is recycled through valve 123 to the vessel 105. The reactor 110 can be isolated from the system by the valve 124 so that after a predetermined amount of time, the reactor can be disconnected from the system and shunted to a different separation module while liquid salt is used to displace liquid sodium present in the vessel 105 and in the titanium particulates forming the cake on the filter 115.

Although the separation systems disclosed herein are batch operations, the valving is such that continuous separations can occur while the reactor is running. A simple system of two or more of the separation systems 10, 80 or 100 permits a reactor continuously to produce the product of the Armstrong reaction.

Although described herein with reference to titanium and sodium, any alkali metal or alkaline earth metal or various combinations thereof may be used as the reductant metal. Any halide may be useful or any combinations of halides may be useful as the vapor which is injected into the liquid metal to cause the exothermic reaction to occur. For reasons of economics, sodium or magnesium are preferred with sodium being mostly preferred. For other reasons, titanium tetrachloride along

with the chlorides of vanadium and aluminum are also preferred in order to make titanium powder or various titanium alloys, the titanium 6:4 alloy being the most preferred titanium alloy presently in use. The 6:4 titanium alloy is 6% aluminum and 4% vanadium with the remainder titanium, as is well known in the art.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WE CLAIM:

1. A method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates, comprising concentrating the metal and salt particulates by removing at least some of the liquid metal, passing the liquid metal or a liquid of the original salt constituent or a mixture thereof at a temperature greater than the melting point of the original salt constituent or mixture thereof through the concentrated metal and salt particulates to further concentrate the metal particulates, and thereafter separating the metal particulates from the remaining original constituents or a mixture of the salt constituent.

2. The method of claim 1, wherein a gel is formed when at least some of the liquid metal is removed.

3. The method of claim 1, wherein liquid metal at a temperature at or above the melting point of the original salt constituent or mixture thereof and contacts the concentrated metal and salt particulates to displace salt particulates and further concentrate the metal particulates.

4. The method of claim 1, wherein a liquid of the original salt constituent contacts the concentrated metal and salt particulates to dissolve or displace salt particulates further to concentrate the metal particulates.

5. The method of claim 1, wherein a liquid mixture of the original salt constituent contacts the concentrated metal and salt particulates to dissolve or displace salt particulates further to concentrate the metal particulates.

6. The method of claim 1, wherein the original constituent of liquid metal is an alkali or an alkaline earth metal or mixtures thereof.

7. The method of claim 1, wherein the liquid original salt constituent or mixture thereof is maintained at a temperature below the sintering temperature of the metal particulates during the further concentration thereof.

8. The method of claim 7, wherein the mixture of the original salt constituent is the eutectic or substantially the eutectic of NaCl and CaCl₂.

9. The method of claim 1, wherein the metal particulates are a Ti or Ti alloy.

10. The method of claim 9, wherein the Ti alloy is 6% Al, 4% V and the remainder substantially Ti.

11. The method of claim 1, wherein the liquid metal is sodium heated to temperature greater than about 600 C.

12. The method of claim 11, wherein the sodium is heated to a temperature greater than about 800 C.

13. The method of claim 1, wherein a liquid of the original salt or a mixture thereof is heated to a temperature greater than about 600 C.

14. The method of claim 1, wherein the metal particulates are Ti or a Ti alloy and the liquid metal is Na and the salt particulates are NaCl.

15. The method of claim 14, wherein the metal particulates are a Ti alloy of 6% Al and 4% V and the remainder being substantially Ti.

16. A method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates, comprising introducing the slurry of original constituents into a vessel having a liquid salt therein wherein layers form due to density differences with the liquid metal being the lightest and the metal particulates being the heaviest increasing the concentration of the metal particulates toward the bottom of the vessel, removing liquid metal from the vessel, separating the concentrated metal particulates with some liquid salt from the vessel, filtering the salt from the metal particulates, and thereafter cooling and water washing the salt from the metal particulates.

17. The method of claim 16, wherein the liquid salt is substantially the same as the salt particulates.

18. The method of claim 16, wherein the liquid salt is a mixture of the salt particulates.

19. The method of claim 16, wherein the liquid salt is an eutectic or substantially the eutectic of the salt particulates.

20. The method of claim 19, wherein the eutectic contains Na and CaCl_2 .

21. The method of claim 16, wherein the liquid salt is maintained at a temperature of less than about 800 C.

22. The method of claim 16, wherein the liquid salt is maintained at a temperature of about 600 C.

23. The method of claim 16, wherein the liquid metal is an alkali or alkaline earth metal or mixtures or alloys thereof.

24. The method of claim 16, wherein the liquid metal is Na or Mg.

25. The method of claim 16, wherein the liquid metal is removed from the vessel by suction with metal particulates being prevented from being removed with the liquid metal.

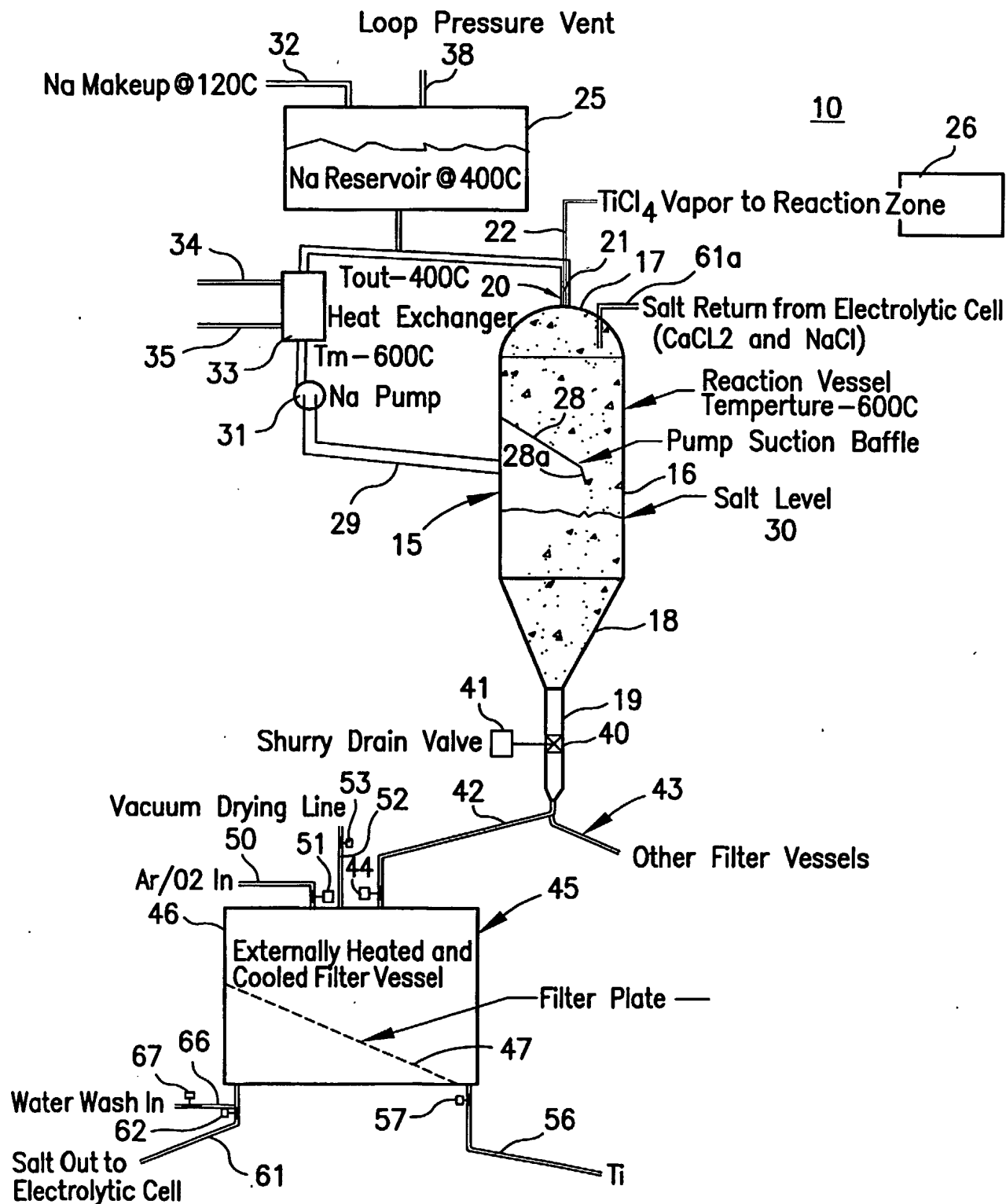


FIG. 1

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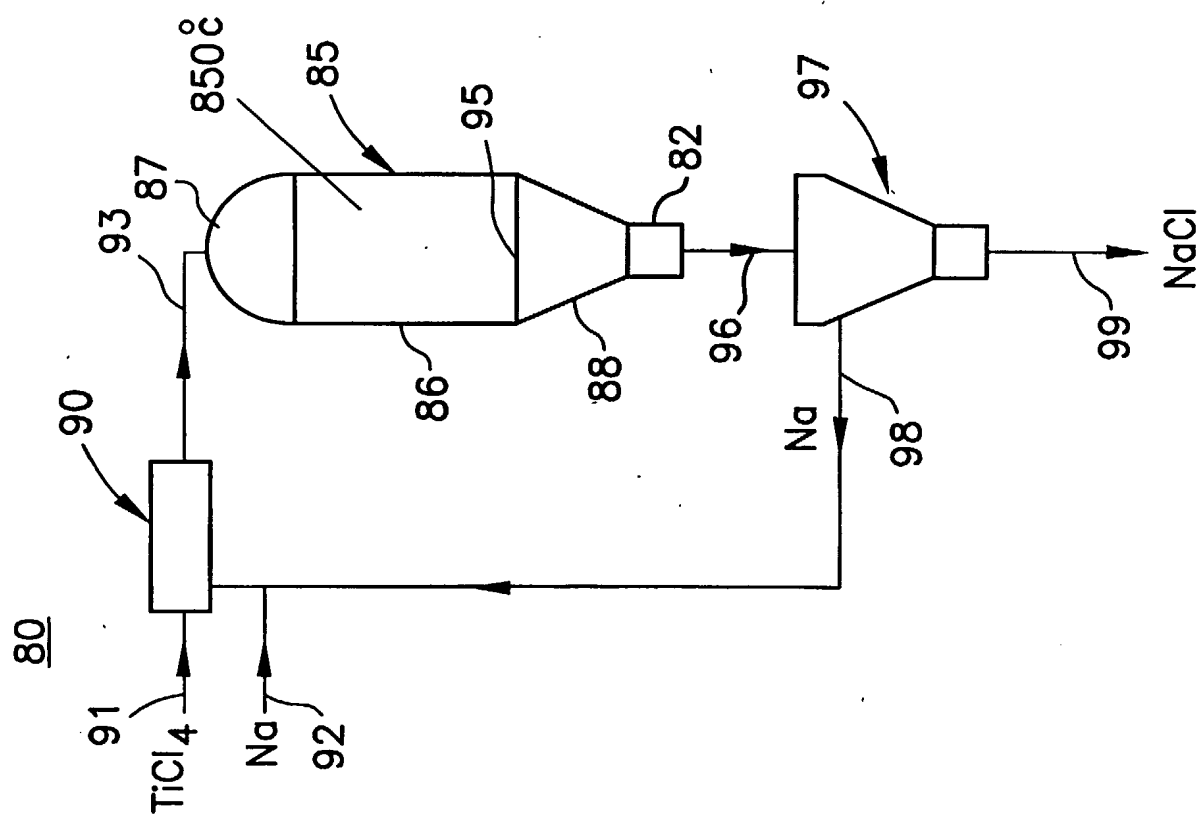


FIG. 2

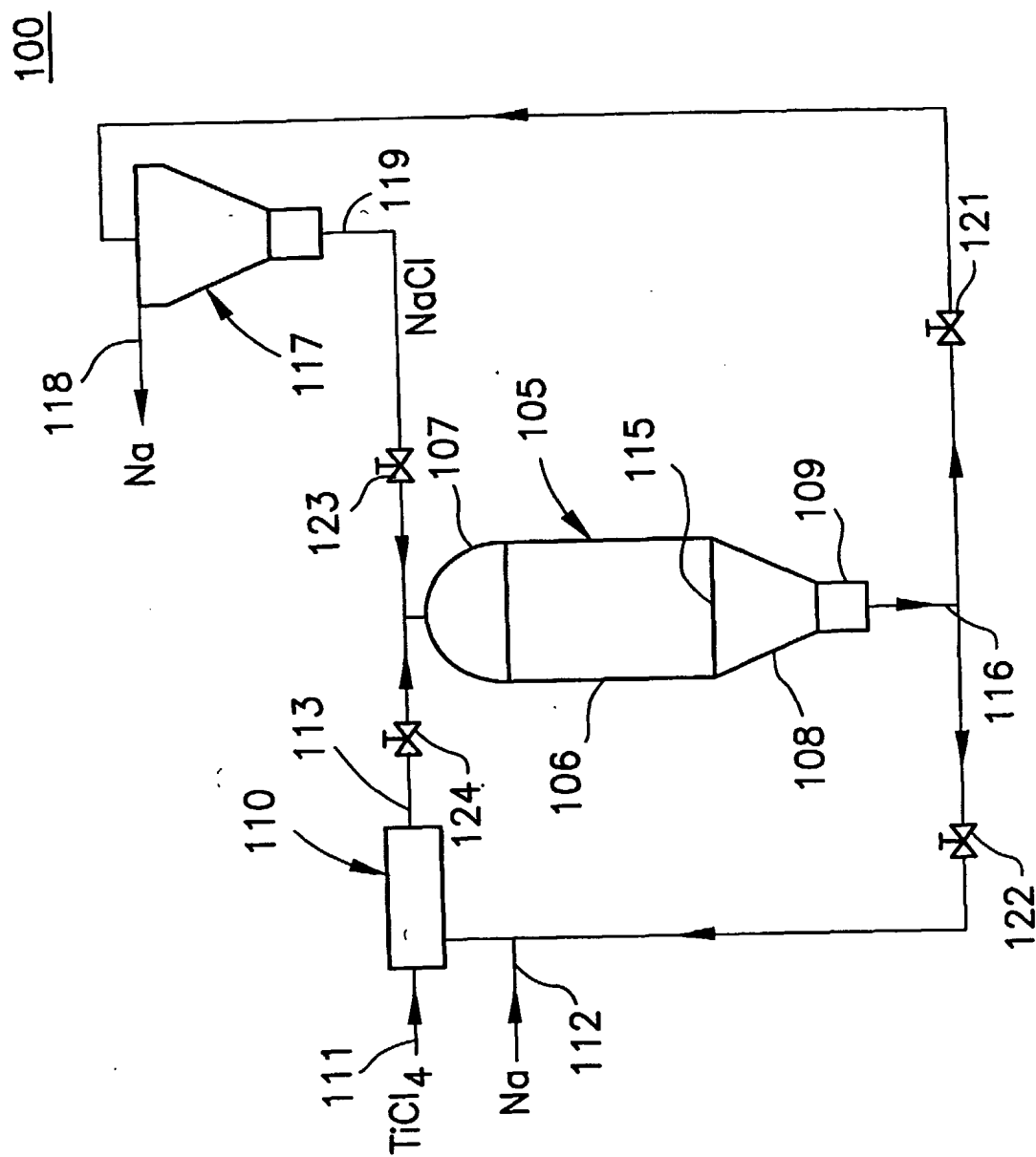


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27785

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B34/12 C22B9/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2 823 991 A (JONAS KAMLET) 18 February 1958 (1958-02-18) claim 1; column 3, lines 33-57 ---	1-25
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A	US 4 379 718 A (GRANTHAM LEROY F ET AL) 12 April 1983 (1983-04-12) -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

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02/02/2004

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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